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(21) International Application Number: PCT/EP86/00370 (22) International Filing Date: 24 June 1986 (24.06.86) (31) Priority Application Number: 21292 A/85 (32) Priority Date: 26 June 1985 (26.06.85) (33) Priority Country: IT (71) Applicant (for all designated States except US): CAPSA-LARM S.A.R.L. [CH/CH]; Via Dufour 2, CH-6900 Lugano (CH). (72) Inventor; and (75) Inventor/Applicant (for US only) : CICUTO, Danilo [IT/CH]; Via Dufour 2, CH-6900 Lugano (CH). (74) Agent: BIANCHETTI, Giuseppe; Studio Consulenza Brevettuale, Via Rossini, 8, I-20122 Milan (IT).	(81) Designated States: AT (European patent), BE (European patent), CH (European patent), DE (European patent), DK, FI, FR (European patent), GB (European patent), IT (European patent), JP, LU (European patent), NL (European patent), NO, SE (European patent), US. Published <i>With international search report.</i> <i>With amended claims.</i>	
(54) Title: MICROINCAPSULATED FLAME RETARDERS (57) Abstract Microencapsulated flame retarders, such as decabromodiphenyloxide, octabromodiphenyloxide, tetrabromoparaxy-lene, hexabromocyclododecane, chlorophosphorated esters in general, tris-(2,3-dibromopropyl)phosphate, trichloroethyl-phosphate, tetrabromophthalic anhydride, tetrabromobisphenol, red phosphorus, ammonium polyphosphate, dibromo-propanol and the like and microencapsulated mixtures thereof. Said flame retarders have an inert and impermeable membrane which isolate each single crystal or liquid drop from the surrounding environment, thus preventing undesired chemico-physical reactions, and eliminating the toxicity of the flame retarders themselves.		

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- 1 -

MICROINCAPSULATED FLAME RETARDERS

The present invention relates to flame retarders for rigid and flexible synthetic foams, binding resins and plastics in general.

Flame retarding agents are known to be substantially
5 ly limited in their possible applications, due to the following drawbacks:

- most flame retarders are more or less toxic and/or corrosive, therefore involving unnegligible problems and difficulties in use and handling. This is the case of
10 tris(2,3-dibromopropyl)phosphate which, in spite of its excellent antifiame properties, at present is not used, due to its high toxicity;
- some flame retarders have stability problems. This is the case of red phosphorus which, in addition to a remarkable toxicity, shows a considerable tendency to
15 spontaneous ignition;
- flame retarders frequently react with the material to be made resistant to fire (for example a polyurethan foam) and said reaction may negatively affect the quality of
20 the manufactured product;
- most of the common flame retarders decompose at a temperature lower than fire decomposition temperature of the treated material, so that, when the material is burning and the flame retarding effect is required, a part of
25 the retarder has been already removed;
- most of usual flame retarders have a limited duration, due to decomposition caused by oxidation and/or photochemical reactions, so that, after some time, the fire

- 2 -

resistance of the treated material decreases.

According to the present invention, in order to overcome the above drawbacks, the various flame retarders are microincapsulated, that is, the particles of said 5 retarders, at the level of each single crystal or microscopic drop, are completely enveloped by an inert and atoxic stable microscopic film, according to various microincapsulation processes, so attaining the following advantages:

- 10 - transformation of any flame retarder, independently on the nature and characteristics thereof, into a simple inert additive till the moment when temperature exerted by fire causes the microcapsules to open, so releasing the flame retarder contained therein, which only from 15 that moment carries on its action;
- possibility to increase flame retarder effectiveness, by incapsulating in one single capsule various compounds having a synergetic action, or using mixtures of microincapsulated flame retarders, which are not compatible 20 under the usual conditions;
- obtaining of a product which is inert at room temperature, but active at the beginning of fire;
- attainment of a product which is safe from risks in handling, being externally non toxic;
- 25 - stability during the time of the retarder characteristics, since the retarder is protected by the membrane from any degradation process.

All of the known flame retarders may be microincapsulated according to the present invention, particularly 30 all the known organic and inorganic halogenated and/or

- 3 -

phosphorated derivatives (used to this scope), such as decabromodiphenyloxide, octabromodiphenyloxide, tetrabromoparaxylene, hexabromocyclododecane, chlorophosphorated esters in general, tris-(2,3-dibromopropyl)phosphate, 5 trichloroethylphosphate, tetrabromophthalic anhydride, tetrabromobisphenol, red phosphorus, ammonium polyphosphate, dibromopropanol and mixtures thereof.

Microincapsulation of said flame retarders may be carried out according to various techniques, such as the 10 method based on gelatins having different viscosities, the one based on gelatins and gum arabic, those based on cellulose derivatives and the like.

The following examples illustrate some of these techniques, without limiting the scope of the invention.

15 EXAMPLE 1

100 Ml of a 10% gelatin solution, 100 g of tetrabromoparaxylene having a particle size of 150 to 300 micron, 100 ml of gum arabic in solution and 300 ml of water were mixed in a vessel and stirred at a temperature from 20 45 to 50°C. The pH of the solution was adjusted to 4.2 and, during stirring, temperature was slowly lowered to 25°, at which temperature a membrane formed around the particles; thereafter the vessel was quickly cooled and stirring was continued during one hour, in order to make 25 the membrane more rigid.

15 Ml of a 25% concentrate of glutaraldehyde was added to harden the membrane and stirring was continued for some hours. The stirring time may be reduced by heating the mass to about 25°C.

30 A dehydrating agent was subsequently added in a

- 4 -

rate equal to 3% by weight of the encapsulated compound, e.g. a compound commercially available under the mark Syloid, said compound being added in order to ease drying, while continuing stirring for about 30 minutes.

5 Water was subsequently separated by filtration or other separation techniques, before drying the microcapsules.

The obtained microcapsules have a weight ratio of 5:1 with respect to the product, i.e. 20 g of material making up the membrane for 100 g of encapsulated tetrabromoparaxylene.

The above cited Example may be carried out varying the compound/membrane ratio in the following percentages: 10:1; 20:1; 40:1.

15 The same Example may be carried out, for all the above cited compound/membrane ratios, using particles of 10 to 1000 microns size. Particularly, when tetrabromoparaxylene is used as flame retarding agent in flexible polyurethane foams, the maximum effectiveness was found for crystal sizes from 50 to 250 microns.

EXAMPLE 2

100 Ml of a 10% gelatin solution was placed in a vessel, at a temperature from 45 to 50°C, under stirring, then 100 g of water, 15 ml of a 5% sodium hexametaphosphate solution and 100 g of decabromodiphenyloxide having particle size of 150 to 300 microns were added, under stirring. pH was adjusted to about 4 and the temperature of the solution was first slowly lowered to 25°C, then quickly lowered to 10°, stirring for one hour at this temperature in order to make more rigid the membrane.

- 5 -

As in Example 1, microcapsule membranes were hardened by addition of glutaraldehyde.

Water separation and microcapsule drying were carried out as described in Example 1.

5 The resulting microcapsules have a membrane/compound weight ratio of 1:10.

As for Example 1, membrane/compound weight ratio as well as microcapsule size may be varied.

EXAMPLE 3

10 250 ml of cyclohexane, 4 g of ethylcellulose and 4 g of carboxylated wax were placed in a vessel. Temperature was raised to 70°C, under strong stirring, to complete dissolution. Then 30 g of ammonium polyphosphate was added, and temperature was lowered to 20°C, continuing stirring.
15 The reaction mixture was filtered, the filtrate was repeatedly washed with pure cyclohexane. Microencapsulated ammonium polyphosphate was then dried in oven, at a temperature not higher than 40°C.

As in the above Examples, membrane/compound ratio
20 as well as microcapsule sizes may be varied.

EXAMPLE 4

100 Grams of red phosphorus is added to 300 g of H₂O, 12 g of urea, 5 g of resorcinol and 40 ml of 40% formaldehyde. The pH is slowly brought down to 1.5 to obtain
25 a polymerization yielding an urea-formaldehyde membrane including red phosphorus. The water is then separated from the obtained microcapsules which are dried.

- 6 -

CLAIMS

1. Microincapsulated flame retarders.
2. Microincapsulated flame retarders as claimed in
5 claim 1, said microincapsulated flame retarders consisting
of any organic or inorganic halogenated and/or phosphorat-
ed derivative utilizable as flame retarder, or of red
phosphorus or mixtures thereof.
3. Microincapsulated flame retarders as claimed in
10 claims 1-2, said microincapsulated flame retarders consi-
sting of decabromodiphenyloxide, octabromodiphenyloxide,
tetrabromoparaxylene, hexabromocyclododecane, chlorophos-
phorated esters in general, tris-(2,3-dibromopropyl)phos-
phate, trichloroethylphosphate, tetrabromophthalic anhy-
15 dride, tetrabromobisphenol, red phosphorus, ammonium poly-
phosphate, dibromopropanol or mixtures thereof.
4. Microincapsulated flame retarders as claimed in
claims 1-3, wherein the coating membrane is one of the
usual coating membranes suited for microincapsulation.
- 20 5. Microincapsulated flame retarders as claimed in
claim 4, wherein the coating membrane consists of gelatins
and derivatives thereof, natural resins and derivatives
thereof, synthetic resins and derivatives thereof, cellu-
lose derivatives, and mixtures thereof.
- 25 6. Microincapsulated flame retarders as claimed in any
one of claims 1 to 5, wherein the membrane is a urea-for-
maldehyde membrane.
7. Microincapsulated flame retarders as claimed in
claim 6, wherein the flame retarder is red phosphorus.

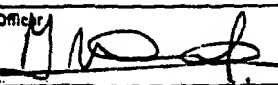
AMENDED CLAIMS

[received by the International Bureau on 15 December 1986 (15.12.86);
original claims 1-7 replaced by amended claims 1-4 (1 page)]

1. Microincapsulated flame retardant compositions characterized in that a flame retardant is coated with an hydrosoluble urea-resorcine-formaldehyde membrane.
- 5 2. Microincapsulated flame retardant compositions according to claim 1 characterized in that the weight ratio urea-resorcine-formaldehyde in the membrane is about 1:2.5:1.
3. Microincapsulated flame retardant composition according to claim 1 wherein the flame retardant is selected in
10 the group consisting of decabromodiphenyloxide, octabromodiphenyloxide, tetrabromoparaxylene, hexabromocyclododecane, chlorophosphorated esters in general, tris-(2,3-dibromopropyl) phosphate, trichloroethylphosphate, tetrabromophthalic anhydride, tetrabromobisphenol, red phosphorus, ammonium
15 polyphosphate, dibromopropanol or mixtures thereof.
4. Microincapsulated flame retardant composition according to claim 1 wherein the flame retardant is red phosphorus.

INTERNATIONAL SEARCH REPORT

International Application No PCT/EP 86/00370

I. CLASSIFICATION F SUBJECT MATTER (if several classification symbols apply, indicate all) *		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC ⁴ : C 08 K 9/10		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
IPC ⁴	C 08 K	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹		
Category ⁹	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	EP, A, 0083768 (KANEKAFUCHI) 20 July 1983, see claim 1; page 2, lines 2-20; examples 1-3 --	1-7
X	EP, A, 0033361 (HOECHST) 12 August 1981, see claims --	1-6
X	US, A, 4208317 (J. CERNY ET AL.) 17 June 1980, see claims 1,3 --	1-7
X	US, A, 4138356 (D. VINCENT ET AL.) 6 February 1979, see claims; column 3, lines 4-33 -----	1-5
<p>* Special categories of cited documents: ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
10th September 1986	20 OCT 1986	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	M. VAN MOL 	

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON

INTERNATIONAL APPLICATION NO. PCT/EP 86/00370 (SA 13708)

This Annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 25/09/86

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A- 0083768	20/07/83	JP-A- 58108248	28/06/83
		US-A- 4493913	15/01/85
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		BE-A- 842698	08/12/76
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